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Civil Engineering Department

Characteristics and Treatment of Wastewater Generated during Underwater Hull Cleaning Operations of U.S. Navy Ships

A Scholarly Paper
Submitted to Dr. A. Davis
In partial fulfillment of the requirements for the
degree of
Master of Science in Civil Engineering

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By
Donna J. Forbes
December 10, 1996

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EXECUTIVE SUMMARY

For the last 15 years the U.S. Navy has been using an underwater diver-operated brush mechanism to clean marine fouling on ship hulls. During this operation, it has been shown that 1 to 2 mils of antifouling paint (which is 40-50 percent cuprous oxide by weight) are removed, resulting in the discharge of up to 1300 pounds of copper into the surrounding surface waters.

This paper reviewed and summarized the recent studies which have been conducted relating to hull cleaning. Among other things, the studies measured dissolved copper in the wastewater ranging from 0.13 mg/L to 4.3 mg/L. These values exceeded the Environmental Protection Agency water quality criterion of 2.9 μ g/L for dissolved copper. Nevertheless, one study even concluded that hull cleaning wastewater may not be toxic to microalgae in the surface waters because the measured dissolved copper concentrations during hull cleanings were lower than the observed IC_{50} values for the microalgae.

Calculations determined the approximate amount of waste that would be generated and the concentration of copper in the waste. From these estimates, four treatment technologies were discussed as possible alternatives for treatment of the wastewater containing antifouling paint: ion exchange, dissolved air flotation, crossflow microfiltration, and living and non-living biological treatment systems.

In addition, an economic analysis was undertaken to compare three levels of treatment: off-site treatment by a commercial facility, on-site treatment to meet minimum sanitary sewer discharge limits using a dissolved air flotation system, and on-site treatment to meet minimum surface water limits using crossflow microfiltration and ion exchange. The economic analysis concluded that leasing the dissolved air flotation system had the lowest annual costs and lowest present worth making it the most economical alternative treatment process.

Lastly, the paper provided several recommendations for further studies which will assist the Navy in the design of an economical and environmentally benign method to successfully manage the treatment of wastewater from pierside hull cleanings.

INTRODUCTION

The U.S. Navy uses an antifouling ship hull coating that is copper-based and is designed to last 15 years. However, significant marine growth has been observed from seven to 30 months after application (Nuckols et al. 1994). Because scheduled drydocking intervals are typically five to seven years for most Navy ships (Valkirs et al. 1994), a method to clean the hull of a ship at pierside is necessary since annual drydocking is cost prohibitive.

Pierside hull cleanings began approximately 15 years ago using a diver-operated brush method. The Navy estimates underwater hull cleaning saves up to $100 million per year in fuel costs because the drag from marine fouling can cause up to a 20 percent increase in propulsive fuel consumption (Bohlander et al. 1992). The hull cleanings not only improve overall ship performance, but also restore the effectiveness of antifouling paint and prevent calcareous fouling which damages the anitcorrosive paint underneath the antifouling paint.

The resulting wastewater from hull cleaning operations consists primarily of sea water, slime, marine growth and anti-fouling paint particles and is discharged directly into the harbor. During hull cleaning, reports estimate one to two mils (0.001 to 0.002 inches) of the 15 mil antifouling paint thickness are removed. Because the antifouling paint is 40-50 percent cuprous oxide, the quantity of copper that is discharged into the harbor as a result of a cleaning can be as much as 165 pounds for smaller Navy ships such as FFG-7 class frigates or as high as 1322 pounds for the largest Navy ships such as CVN-68 Nimitz class carriers (Nuckols et al. 1994).

Because the water quality of bays and estuaries is under increasingly stringent environmental regulation and concern, the Navy foresaw that hull cleaning discharges may eventually be regulated. For this reason and for other long term ship hull maintenance reasons, the Naval Warfare Surface Center (NSWC) undertook the development of an alternative method to clean the hulls and to collect and to treat the resulting wastewater, while at the same time, to have a method to collect important data for future drydockings. The new hull maintenance system currently in design, test and evaluation is called the

Automated Hull Maintenance Vehicle (AHMV). Depending on the level of treatment economically achievable, the wastewater will either be treated and discharged back into the harbor or pretreated and discharged into the sanitary sewer system for further treatment.

The purpose of this paper is to review and to summarize the studies which have been conducted relating to hull cleaning, to discuss alternatives for treatment of the wastewater containing antifouling paint and to provide recommendations for further studies that will assist the Navy in improving the design of an economical and environmental benign method to successfully accomplish pierside hull cleanings. In addition, an economic analysis of three alternative treatment methods will be presented: one alternative which will allow discharge of the effluent into the surface waters; one which will allow discharge of the effluent into the sanitary sewer system, and one which will truck the wastewater to a commercial treatment plant. These analyses will assist the Navy in deciding a cost-effective level of treatment for this wastewater.

GENERAL ISSUES

There are over 130 hull cleanings in the United States by the Navy per year. If it is assumed that the average hull surface area is 36,000 square feet and an average of 1 mil of paint is removed, then approximately 150 pounds of copper are currently discharged into the surface waters per cleaning. Although eliminating this pollution source completely would be best, this is not a practicable solution for the near term; therefore, some level of treatment of the effluent generated by the AHMV is required. The level of treatment should not be solely an economic decision, but one which also considers potential liabilities. For example, the convenience of contracting with a third party to treat the effluent offsite or to treat the effluent at existing Navy facilities may out-weight the liabilities of managing a new treatment process and the associated NPDES permit for discharging the effluent directly into surface waters.

ELIMINATING THE SOURCE OF POLLUTION

Ideally, an environmentally risk-free coating would be developed which could achieve at least the same results available with current methods. The Navy and private manufacturers continue research and development of better coatings which are at least equally reliable and environmentally benign. But, even if such a coating was developed and approved, it would still take many years to recoat all Navy ships.

The recoating of a hull normally takes place at the same drydocking when other extensive repairs are planned. Approximately five percent of the 350 naval ships are undergoing this overhaul at any time. So, recoating the entire naval fleet could take up to 20 years. Therefore, an intermediate solution is necessary while long term alternatives are investigated and developed.

The average number of hull cleanings over the last three years, by location, is reported in Table 1 (McCue 1996).

Table 1. Three Year Average Number of Hull Cleanings.

Location	Percent of Total Cleanings	Total for the Last Three Years
Southern California	37	151
Norfolk	21	86
Texas	13	52
Hawaii	8	33
Georgia/Florida	6	27
Carolinas	6	24
Northern California	4	17
Other	5	20

HULL MAINTENANCE VEHICLE

The current pierside hull cleaning device is a diver-operated machine called the SCAMP. The SCAMP removes marine fouling mechanically using three rotating brushes and producing a six foot wide swath. The SCAMP attaches to the ship hull by suction created from an impeller located in the center of the SCAMP which pumps seawater outward. A diver holds the SCAMP and "drives" it across the hull surface.

The alternative AHMV under current study significantly reduces or eliminates all copper discharges to the harbor during in-water cleanings. Attached to the AHMV is a remotely operated vehicle (ROV) which self-navigates the AHMV across the ship hull and, since experience indicates only about 20 percent of the hull has marine fouling, the AMHV design has sensors which detect fouling and activate the cleaning brushes only on the affected areas. This not only reduces the amount of copper discharged directly into the harbor, but also reduces the life cycle maintenance costs of the ship by removing less antifouling paint. Figure 1 is an artist's concept of the sensors, cameras, thrusters and cleaning brushes of the AHMV.

The AHMV will not only improve maintenance of antifouling paint, its sensors will measure and store data on paint thickness, hull electropotential and hull plate thickness as the vehicle transverses. For example, the paint thickness data will help to determine if antifouling paint needs to be applied at a planned dry docking and the electropotential readings will help to determine if the anodes of the impressed current cathodic protection system are working properly. The hull plate thickness data will detect thin areas that may require maintenance or repair at the next planned drydocking (Bohlander et al. 1992).

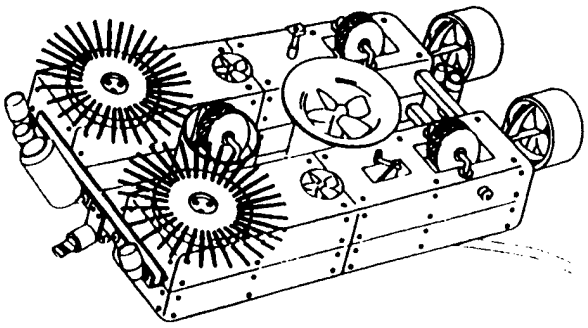

Figure 1. Brush Cleaner Configuration of the AHMV (Bohlander et al. 1992).

SANITARY SEWER VERSUS SURFACE WATERS DISCHARGE

There are many professional opinions on the level of treatment that should be required of the hull cleaning wastewater. Because of their industrial nature, the naval shipyards already have treatment processes available for the removal of metals and prefer these processes be used to treat hull cleaning wastewaters, if possible. These processes are know to successfully treat industrial waste to the limits required in their respective areas, and the Navy already has the trained operators. Generally, the shipyards pay the local sanitary jurisdictions to accept saltwater waste and, in some cases, have paid for a portion of the sanitary sewage treatment plant construction or expansions. However, the naval stations which currently do a majority of the hull cleanings for the Navy and pay local sanitary jurisdictions to process their wastewater, do not have treatment processes readily available. There is some feeling that the pretreatment to remove copper will also remove most of the organics which will make the wastewater "too clean" and unacceptable by local sanitary sewer authorities. In addition, there is continued pressure from local sewage treatment entities for the Navy to reduce the daily flow of all wastewaters.

At the busiest naval operating base, Norfolk, Virginia, a treatment plant is under construction that will process all bilge water at the Norfolk piers. The construction also includes a system which will collect the bilge water at the ship. Construction of the plant and collection system is scheduled to be completed in 1998. The system was designed for a "growing" Navy and will be able to handle 750,000 gallons per day. However, Navy experts believe it will only reach half of its capacity which would allow this treatment plant to be used as an option for the Norfolk area to treat hull cleaning wastewater. The Navy anticipates that the cost for wastewater treatment at this facility will be $0.01 per gallon (Lee 1996). A useful tool for evaluating treatment technologies for hull cleaning operations would be a summary of all existing or future treatment systems available at all locations were U.S. Navy ships are homeported in the United States.

WASTEWATER CHARACTERISTICS

In 1984 the Navy began testing a copper ablative paint for antifouling protection and it is now in standard use for U.S. Navy ships. Although the copper ablative paint performs better than the former paint, it is softer and, as a result, more paint is removed during a hull cleaning.

The material safety data sheet (MSDS) for the antifouling paint is shown in Appendix A. The percent by weight of the hazardous ingredients are given. The two highest quantities of hazardous ingredients are copper oxide and zinc oxide with copper twice the quantity of zinc. In addition, National Pollution Discharge Elimination System (NPDES) permit limits managed by the Navy have a limit for zinc that is 10 to 50 times higher then the limit for copper (NRaD, 1995). Therefore, this paper will focus on the copper limits because the required percent removal is higher than zinc and because the technologies addressed should consecutively remove zinc.

The Navy has completed three studies on hull cleaning wastewater. The studies have focused on the levels of copper (total and dissolved), the toxicity of the copper in the wastewater and background measurements of copper. The studies provide measurements of dissolved copper in the wastewater that range from 0.13 mg/L to 4.3 mg/L, provide background measurements of copper that exceed the EPA water quality criterion of 2.9 μ g/L for dissolved copper, and provide data that the hull cleaning wastewater may not be toxic to microalgae.

SAN DIEGO STUDY 1994

A field study performed in San Diego Bay evaluated the environmental risks from in-water hull cleaning and was completed by Naval Command, Control and Ocean Surveillance Center (NCCOSC) which has an extensive database on San Diego Bay from the many water quality, biological, and ships husbandry studies . Because of the escalating concern over the bays and estuaries throughout the United States, it is felt that the use and maintenance of antifouling paints will be regulated in the future by restricting release rates and discharge limits and increasing debris cleanup and monitoring requirements.

The NCCOSC study had two objectives: to define the overall environmental loading and mass balance of copper in typical Navy harbor environments and to evaluate the magnitude and fate of those materials derived from in-water hull cleaning operations; to examine the possible toxicity of hull cleaning by-products of copper ablative coatings and to identify the biological effects of chemical species of this material (Valkirs et al. 1994).

Detailed measurements and sampling were completed during six in-water hull cleanings that took place between August 1991 and July 1993. Both real time measurements of the effluent plumes during the cleaning were monitored and harbor-wide background levels and ambient distribution measurements were taken when there were no hull cleanings in progress. The background and ambient levels of copper were compared to studies completed by the Naval Undersea Center (NUC) in 1974 and 1975 which were prior to underwater hull cleaning operations, and to a study completed by the National Oceanic and Atmospheric Administration (NOAA) from 1984 to 1989.

The three primary by-products of hull cleaning were evaluated: dissolved copper, particulate copper and organic fouling debris (Valkirs et al. 1994). Dissolved copper is defined as copper that will pass through a 0.45 μ m filter; the largest releases occurred during and shortly after a hull cleaning operation. Dissolved copper is the bioavailable form of copper which is considered the most toxic form. Particulate copper is the copper in paint chips that settles to the bottom or is sometimes suspended in the water column for varying lengths of time. The effects of particulate copper will depend on the amount that sediment-dwelling organisms consume. Organic fouling debris is present on or in sediments near hull cleaning areas. The effect of this fouling debris is autrophic consumption of oxygen and elevated nutrient levels during the decomposition of the organics.

Most studies measure copper of all species and consider all copper species responsible for any toxic effects. However, the NCCOSC study noted that there is a difference between the toxicity of biologically available copper and of total copper. Normally, copper is bound in complex organic compounds or adsorbed onto particulate material, therefore, total copper measurements may be high, but bioavailable copper may

be low (Valkirs et al. 1994). The most recent EPA interim guidance for water quality criterion for metals in marine waters suggests that the criterion not be based on the simple measurement of total recoverable metals. Instead, EPA recommends that the criteria be based on studies that compare toxicity results for total metal versus dissolved metals and toxicity results for laboratory waters versus site specific waters in order to develop metal criteria (U.S. EPA 1992). Most states have not yet endorsed this EPA recommendation and are still operating under the 1984 EPA criterion which is a one-hour average concentration limit not to exceed 2.9 μ g/L of total copper (U.S. EPA 1985).

Water samples were taken in close proximity to naval vessels during in-water hull cleaning operations and later compared to background copper concentrations. Table 2 lists the measurements and tests conducted during the study.

Table 2. Test and Measurements Completed by NCCOSC.

Component	Technique for Measurement
Total dissolved copper	standard atomic absorption techniques
Copper speciation (20 percent of the samples)	electrochemical techniques with anodic stripping voltametry
Toxicity (50 percent of the samples)	standard laboratory bioassay test
Total particulate copper	particles larger than 0.45 μm in size

The following are the conclusions from the study (Valkirs et al. 1994).

- Of 58 background measurements taken from May 1991 to February 1993 in the Navy pier areas of the San Diego Bay, only 24 (40 percent) were at or below the existing EPA water quality criterion for dissolved copper of 2.9 μ g/L.
- The background copper concentrations when compared to the NUC and NOAA studies were fairly constant over the last 10 years in spite of underwater hull cleaning operations.

Table 3. Background Measurement of Copper.		
Year	Water Column	Sediments
1975	3-16 μ g/L	40-360 mg/kg
1980s	2.2-23 μ g/L	92-241 mg/kg
1993	average 5.8 μ g/L	132-268 mg/kg

- While the dissolved copper concentrations are elevated during hull cleaning operations near the ship, samples taken in the same location 30 minutes to two hours after cleaning operations had ceased showed that the levels of dissolved copper returned to near ambient background levels of 2.5 to 8.7 μ g/L.
- The elevated levels of dissolved copper were observed from two to 96 meters away from cleaning operations and the concentrations varied from 2 μ g/L to 20 μ g/L during the hull cleaning operations.
- Fifty to eighty percent of the copper discharged to the harbor during an in-water hull cleaning operation is particulate in the form of paint chips and is non-toxic to marine organisms.
- Dissolved copper concentrations in the vicinity of hull cleaning operations (2 μ g/L to 20 μ g/L) do not appear to be toxic to microalgae since the observed IC_{50} value (50 percent inhibition of algal growth at a copper concentration) were 42 to 50 μ g/L of dissolved copper.
- Due to the high percentage of clay (average of 26 samples was 18 percent clay) found in the sediments of the San Diego Bay, it is likely that the copper leached from paint chips will not be bioavailable , but instead readily binds with the clay.

It has been estimated the input of copper in San Diego Bay from pleasure, military and commercial vessels due to antifouling paint is 56 metric tons annually (Valkirs et al. 1994). Although the Navy study indicates there is minimal effects from the copper, the EPA water quality criterion will be very difficult to meet with this continuous level of

deposit of copper. The Navy projects that underwater hull cleaning operations is one point source that regulatory agencies will look to regulate in order to reduce copper levels in bays.

NAVAL SURFACE WARFARE CENTER (NSWC) STUDY 1995

The purpose of this study completed by NSWC was to identify the chemical compositions of the effluent generated from hull cleaning operations. NSWC requested the capture of the wastewater generated from underwater hull cleaning by the cleaning contractor, Seaward Marine Services. In April 1995, 300 gallons of effluent from the SCAMP were captured during the underwater hull cleaning of the USS Harlan County in Norfolk, VA. The effluent was captured near the discharge plume using a 4-inch diameter 300-foot hose, pumped pierside with a submersible, hydraulic centrifugal pump and stored in 55 gallon, high density polyethylene shipping containers. Once the wastewater was captured, three companies with experience in metal removal were contracted to analyze the composition and to attempt to remove the dissolved copper and zinc to 1 mg/L each using resin ion exchange. In addition, two labs were contracted to evaluate the composition of the wastewater (Nuckols et al. 1995). Table 4 shows the analyses of the wastewater before treatment that was received from the laboratories and contractors (Nuckols et al. 1995). All tests were completed one week to three months after the hull cleaning operation. The three companies had good results treating the wastewater with an ion exchange system. However, the contractors felt additional studies ought to be conducted because of the low concentration of copper in the wastewater tested.

Table 4. Chemical Assessment of SCAMP Effluent - As Received (undigested).

Component (mg/L)	Company1	Company2	Company3	Lab1	Lab2
Zn	0.62	--	--	5.0	--
Cu	0.22	0.3-0.4	0.36	0.07	0.10

Note: Company1 also tested for other components (mg/L); Na=6683, K=254, Mg=899, Fe=0.14, Ca=290, pH=7.57

Surprisingly, all contractors found the concentration of copper in the wastewater below 1 mg/L without applying treatment. One contractor even attempted to elevate the copper and zinc levels to 20 mg/L for each metal in order to test their selective ion exchange resin. Although it successfully elevated the zinc, it could only elevate the copper to 2 mg/L because of the low solubility of copper in seawater in the pH range of 7.5 to 8.0 (Nuckols et al. 1995). Another contractor, Mobile Processing Technology, filtered the wastewater with different size filters then measured the copper levels of the effluent levels and of the residue collected. Mobile Processing Technology used a colorimetric method sensitive in the range of zero to 210 μ g/L to measure the levels of copper (Nuckols et al. 1995). The results from Mobile Processing Technology are presented in Table 5.

Table 5. Analytical Results from Mobile Processing Technology.

Sample	Cu
Wastewater as received	356 μ g/L
Wastewater after 24 hrs	231 μ g/L
Filtered residue + H_2SO_4	28 mg/L
11 μm - 5μm + 1μm + 0.45μm	<0.01 μ g/L**
11 μm filter	<0.01 μ g/L
11 μm + H_2SO_4	<0.01 μ g/L

**The Hach is not sensitive below measurements of this amount

In order to fairly evaluate the results of the USS Harlan, two additional hull cleanings were analyzed. NSWC wanted to determine if there were any wide variations in wastewater characteristics at each hull cleaning and to evaluate the wastewater composition over a period of time to determine if some dissolved copper and zinc precipitate out of solution. Therefore, all samples were taken pierside, but some were measured immediately and some were monitored over a two week period at Annapolis, Maryland.

The measurements were completed with a portable spectrophotometer test kit by the Hach Company. The total dissolved copper was measured using the EPA approved Bicinchoninate Method (Hach Company 1992). This method uses a reducing agent converting all Cu^{-2} to Cu^{+1}, an acid reagent reacts with the Cu^{+1} producing a purple-colored complex, and a measurement is taken from the spectrophotometer.

The free copper ions were measured using the Porphyrin Method (Hach Company 1994). First, the sample was split. One split was used to calibrate the spectrophotometer and the other split was used to take the free copper measurement. The spectrophotometer was calibrated by forcing the free copper of one split to complex with a masking agent, then porphyrin (a buffer and reducing agent) was added and the "zero" reading was taken. For the second split, no masking agent was added. Instead, the porphyrin was added, reacting with the free copper forming a pale yellow complex and a measurement was taken from the spectrophotometer. The yellow color is the most efficient light absorbent at a wavelength of 425 nanometers. Before the wastewater was measured, both methods were tested using a copper standard solution of 1 mg/L and both measurements were within 5 percent of the standard. The results are shown in Table 6 (Nuckols et al. 1995).

Table 6. Analytical Results from Naval Surface Warfare Center.

Test	USS George Washington July 7, 1995		USS Monterey August 10, 1995		USS Harlan County 3 months after cleaning	
Water Temp. C	26.0		27.5		--------	
Water pH	8.0		7.96		--------	
Water s.g.	1.017		--------		--------	
Total Dissolved (mg/L)	Unfiltered 1.23 ± 0.15	Filtered* 0.41 ± 0.03	Unfiltered 0.55 ± 0.01	Filtered* 0.31 ± 0.00	Unfiltered 0.13	Filtered* <0.01 μ g/L
Free Copper (mg/L)	$\rangle$ 0.23	$\rangle$ 0.23	0.28	0.26	0.02	<0.01 μ g/L

*The filter pore size was 10 μ m.

The results shown in Table 6 provide three observations. First, by simple filtration the effluent can be immediately discharged into most sanitary sewage systems since the level of copper is already below 1 mg/L. Second, the total dissolved copper

differs significantly between the USS George Washington and the USS Monterey. This difference may result from several factors including the condition of the paint, the amount of marine fouling on the ship, the amount of paint removed or the rate the diver performs the SCAMP movement. Lastly, dissolved copper concentration variations between the effluent immediately measured and the effluent stored for three months support the theory that copper attaches to solid material in water and could later be treated using a 10 μ m filter to none detectable levels.

In addition to the measurements taken pierside, the total dissolved copper levels were monitored for 17 days and the levels of copper were measured after adding solid matter. Unexpectantly, the dissolve copper levels were still significant after storage and even increased during the 17 days. The study attributed this to dissolving particulate copper and the unavailability of solid matter from settling for the dissolved copper to complex. Measurements showed that 60-80 percent of the dissolved copper was free copper (Nuckols et al. 1995)

Two types of solid matter were added to two separate samples to observe the adsorption of the dissolved copper. In the first sample, 20 grams of clay were added to 400 mL of unfiltered effluent from the USS George Washington. After 18 hours, the dissolved copper levels were reduced 68 percent. In the second sample, 20 grams of algae were added to 400 mL of unfiltered effluent. The algae test was repeated two additional times and measurements of dissolved copper levels below 0.3 mg/L after two hours were found for all three samples (Nuckols et al. 1995).

NORFOLK FIELD STUDY 1996

In September 1996, the firm designing the AHMV and Mobile Process Technology were contracted to study the capture and pumping of the wastewater generated by the SCAMP and to treat the wastewater with microfiltration and ion exchange. In addition, the Navy captured four 55 gallon drums of the wastewater to send for analysis and treatment by the Department of Energy and the Smithsonian Institute. The Navy also analyzed the wastewater with the Hach test kit on the pier. The hull cleaning was for the USS Nashville homeported in Norfolk, Virginia.

The average flowrate of the wastewater to the pier was 160 gpm through a four inch, 150 foot hose. The results of the wastewater analyses for dissolved copper and zinc concentrations are in Tables 7 and 8.

Table 7. Dissolved Copper & Zinc Concentrations, September 25, 1996.

Ambient Measurements: Cu = 0.3 to 1.3 μ g/L; Zn = 0.01 mg/L; T = 74° F

Level of Treatment	Cu	Zn
No treatment sample 1	1.5 mg/L	1.63 mg/L
No treatment sample 2[1]	4.3 mg/L	2.2 mg/L
0.2 μ m ceramic filter	96.7 μ g/L	70 μ g/L
0.2 μ m filter + ion exchange	5.8 μ g/L	10 μ g/L

Table 8. Dissolved Copper & Zinc Concentrations, September 26, 1996.

Ambient Measurements: Cu = 0.6 to 12 μ g/L; Zn = 0.04 to 0.14 mg/L

Level of Treatment	Cu	Zn
0.2 μ m metal filter	192 μ g/L	-----
0.2 μ m metal filter	183 μ g/L	0.11 μ g/L
0.2 μ m filter + ion exchange	<0.01 μ g/L	0.07 μ g/L

The results show that NPDES permit limits for copper shown in Table 9 can be achieved with microfiltration and ion exchange and that sanitary sewer limits for copper from Table 10 can be achieved with microfiltration.

[1] Due to the amount of solids, the sample had to be filtered through a coffee filter in order to get a reading on the Hach kit.

REGULATIONS

Unlike waste streams generated from drydock operations which are regulated, the wastewater from underwater hull maintenance is currently not regulated. The current NPDES permit for Puget Sound Naval Shipyard (PSNSY), Long Beach Naval Shipyard (LBNSY), Norfolk Naval Shipyard (NNSY) and Naval Base San Diego (NBSD) are summarized in Table 9. Two additional naval industrial areas, Portsmouth Naval Shipyard and Pearl Harbor Naval Shipyard, do not have copper NPDES limitations.

Table 9. NPDES Copper Limitations at Four Naval Bases.

Location	Monitoring	Water Quality Objective	Frequency
PSNSY (NRaD, 1995)	Monthly average Daily average	19 μg/L 33 μg/L	Weekly w/grab sample Total recoverable copper
LBNSY (NRaD, 1995)	Instantaneous maximum	2.7 μg/L	Semiannually Grab sample
NNSY (NRaD, 1995)	Daily maximum	335 μg/L	Quarterly 24 hour composite Total recoverable copper Dissolved copper
NBSD (Gordon, 1996)	6-month median Daily maximum Instantaneous maximum	5 μg/L 20 μg/L 50 μg/L	

In contrast, the sanitary sewer limits for copper are listed in Table 10.

Table 10. Sanitary Sewer Limitations for Copper.

Location	Cu Limit
Norfolk	0.8 mg/L
Puget Sound	5.2 mg/L
San Diego[2]	4.5 mg/L
Portsmouth	1.0 mg/L
Pearl Harbor	3.38 mg/L

Although the NPDES permits are currently not for hull maintenance cleaning streams, the Navy's goal is to maintain these limitations for all pierside streams. In the future, the new AHMV system will create a point discharge and may require a NPDES permit. However, the Navy is attempting to regulate hull maintenance with the Uniform National Discharge Standards (UNDS), which was signed and became law on February 10th, 1996 as part of the Fiscal Year 1996 National Defense Authorization Act (U.S.Code 1996). UNDS requires the Department of Defense (DoD) and the EPA to jointly write the regulations for discharges from vessels of the armed forces. UNDS is currently under a five year implementation plan.

Navy ships have a number of different discharges: point discharges for example include sewage, graywater, bilge water, cooling water, ballast water and boiler blowdown, while nonpoint discharges include stormwater runoff, washdown runoff, and leachate from hull coatings. According to 40 CFR 122.4, the EPA regulations implementing the NPDES program provide that discharges "incidental to the normal operation of vessels" do not require NPDES permits. To date, only sewage is regulated by requiring marine sanitation devices (MSD) which prevent the discharge of untreated or inadequately treated sewage.

Because Navy ships operate in coastal waters and ports throughout the United States, the Navy seeks to maintain good relations with local authorities by complying with

[2] North Island. San Diego, CA is required to meet metal finishing standards for a monthly average of 2.07 mg/L.

local and state laws. But, to comply with all the local and state laws on a case-by-case basis has been a confusing and frustrating experience for operational commanders. A uniform national standard would enable the Navy to design and build ships and train crews to comply with the known national requirements while operating from port to port.

The purpose of the UNDS is to enhance the operational flexibility of vessels of the armed forces domestically and internationally, stimulate the development of innovative vessel pollution control technology, and advance the development by the U.S. Navy of environmentally sound ships (U.S. Code 1996). Because U.S. Navy ships are mobile pollution sources, the UNDS will allow the Navy to both complete its mission and comply with one regulation that is accepted throughout the United States. The standards developed will be a collaborative effort by the Departments of the Navy and Defense, the EPA, other federal agencies, states and environmental interest groups. The Assistant Secretary of the Navy for Installations and Environment believes UNDS will be a "win-win" product for environmental protection and national security (Quinn 1996).

TREATMENT PROCESSES

This section will discuss four issues associated with treatment of hull cleaning effluents including: the options for capturing the waste; parameters and assumptions used to estimate the volume of wastewater, amount of time for the AHMV to transverse the hull and concentration of total copper; a study completed by the National Steel and Shipbuilding Company on treatment of drydock effluent; and four possible treatment processes for the wastewater.

COLLECTION OPTIONS

In August 1994, a study was completed by the U.S. Naval Academy and the Naval Surface Warfare Center (NSWC) which investigated the collection system for the AHMV. The study compared four alternatives which are illustrated in Figure 2. The costs in the study assumed that the AHMV cleaning brushes operate 100 percent of the time and produce a flowrate of 100 gallons per minute (gpm) (Nuckols et al. 1994).

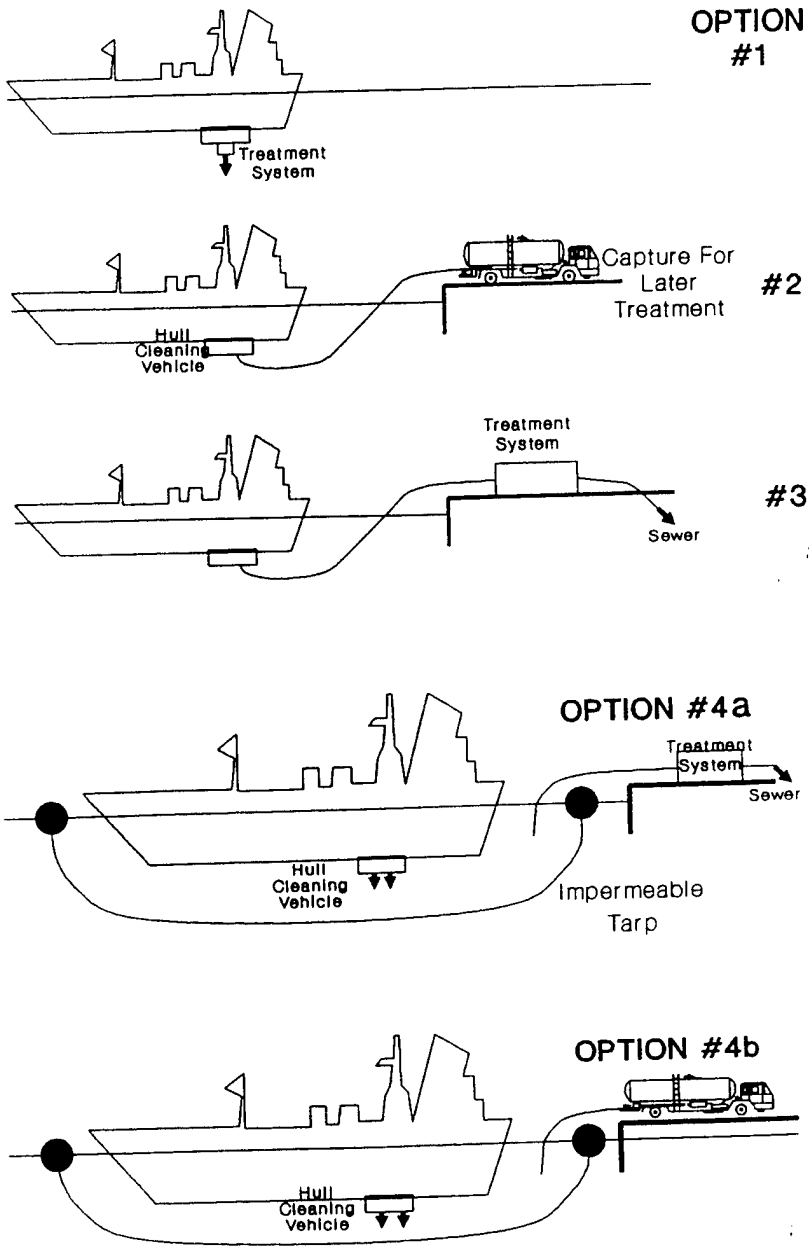

Figure 2. Effluent Capture Options for the AHMV (Nuckols et al. 1994)

Option 1 is a wastewater treatment system attached directly to the AHMV. The advantage of this arrangement is the AHMV would not be encumbered with an external piping system that would deliver the wastewater to the surface. Consequently, less power would be required because there is no drag caused by piping. The study concluded that the wastewater treatment technologies available to handle the flowrate and removal efficiency would likely be several times larger than the size of the AHMV, making the self-contained treatment not practical.

Option 2 is a wastewater pumping and piping system to deliver AHMV effluent to tankers on the surface which would deliver the wastewater to commercial treatment facilities. This system requires less manpower , but would be costly due to the transportation and commercial treatment expense. The estimated treatment cost is $0.14 per gallon, not including transportation (Nuckols et al. 1994). A complete cleaning of one Navy ship would range between $15,800 to $67,000 for effluent disposal depending on the wetted surface area of the ship. For example, a cruiser cleaning would generate 113,500 gallons of wastewater , but cleaning a large ship such as an aircraft carrier would generate 478,000 gallons of wastewater.

Option 3 is a pierside processing plant. It was estimated that a skid-mounted processing plant would cost about $0.04 per gallon (Nuckols et al. 1994). Though option 3 would require an initial capital investment on the part of the Navy, the pierside system would save in excess of $11,000 to $47,800, plus transportation cost for every usage.

Option 4 consists of a impermeable tarp supported by surface buoys. This system separates the hull cleaning and the wastewater treatment systems. First, the hull would be cleaned with the AHMV, the tarp would enclose all the waste and, lastly, the water would be pumped to the surface for either treatment on pierside (4a) or for transportation to a commercial treatment facility (4b). The AHMV would require less power because there is no wastewater pumping and piping system and the discharge rate of the AHMV would not have to meet the surface pumping rate or treatment processing rate. However, the process was rejected as not feasible because of the large volume of water which must be treated. It was estimated that a medium sized ship such as a cruiser would require the

treatment of 2.8 million gallons of wastewater and a large ship such as a aircraft carrier would require the treatment of 19 million gallons of wastewater.

The most cost effective option appears to be the pierside wastewater treatment process, option 3. A pierside process needs to be small enough to fit on a tractor trailer because pier space is limited and other higher priority pier activities relating to operation, maintenance or resupply could interrupt hull cleaning.

An economic analysis should be completed evaluating options 2 and 3 when only 30 percent of the hull is cleaned using the AHMV because it is estimated that only 20 percent of the hull requires the removal of marine fouling and 30 percent provides a 1.5 safety factor. The cost of capital investment and sludge management may not be as cost-effective as trucking to a wastewater treatment plant when less volume needs to be treated. In addition, the study did not provide the source for the prices that were used and it was not clear if the $0.04 per gallon for treatment includes sludge handling. Also, the average cost to treat wastewater at commercial treatment plants in the Norfolk area is $0.25 per gallon and the cost for the Navy to treat its own wastewater at the local municipal treatment plant is $3 per 1000 gallons ($0.003/gal) (Lee 1996).

NATIONAL STEEL AND SHIPBUILDING COMPANY (NASSCO)

NASSCO completed a study that summarized comments and results from three earlier studies on possible technologies for the treatment of wastewater from hull cleaning in drydock using hydroblast. The drydock wastewater is different from the pierside wastewater for two reasons: drydock cleaning uses freshwater and drydock cleaning does not use brushes. However, the results and comments from the studies are useful for evaluating treatment technologies for removing copper to sewer or surface water requirements.

Two important conclusions on the treatability of hydroblast wastewater are (NASSCO 1995):

- Removing the suspended solids results in the concentrations of copper, lead and zinc acceptable for sanitary sewer discharge.

- Removing dissolved metals will be required in order to achieve acceptable levels for direct discharge into the harbor.

The results of pilot plant studies completed by the Municipality of Metropolitan Seattle Water Pollution Control Department on drydock effluent are presented in Table 11 (NASSCO 1995).

Table 11. Summary of Copper Removal from Pilot Plants by Metro Seattle.

Treatment Technology	Untreated Sample (mg/L)	Treated Sample (mg/L)	Removal (%)
Mixed Media Filtration	0.12	0.02	83
Ultrafiltration	5.3	0.1	97
Media Precoat Filtration	3.1	2.5	19
Settling/Filtration Mixed-media 1	35.0	0.22	99
Settling/Filtration Mixed-media 2	2.5	0.44	82
Chemical Flocculation Alum & Lime	42.0	0.6	99
Chemical Flocculation Cationic Polymer	16.0	0.7	95
Dissolved Air Flotation Alum Flocs	1.8	0.6	67
Induced Air Flotation Alum Batch	6.6	0.15	96

The best removal results used chemical flocculation with alum and lime addition; however, none of the treatment technologies removed to the Navy NPDES permit requirements on Table 11.

EFFLUENT PARAMETERS AND THEORETICAL COPPER CONCENTRATION

In order to select a treatment technology, several parameters must be assumed or predicted. The assumptions that will be made in order to predict the copper concentrations, volume of wastewater and cleaning time are:

Flow rate = 200 gpm (Mehnert 1996)

Cleaning rate = 2,000 ft^2/hr (Nuckols et al. 1994)

Removal of paint during cleaning = 2 mil (Nuckols et al. 1994)

Amount of surface area cleaned = 30 percent (safety factor of 1.5) = f_s

AHMV operates 6.5 hours per day allowing for mobilization and demobilization.

Paint on the hull of the ship is BRA 540 which the Navy currently applies to ships (Nuckols et al. 1994).

Weight = 18.5 lb/gallon of paint

Specific Gravity = 2.22 (wet paint)

Percent of CuO = 45

The following formulas are taken from the 1995 Nuckols study, however, the calculations are completed using the assumptions above. Nuckols' study assumed 40 percent of the surface area cleaned and a flowrate of 100 gpm. The formulas employed in a spreadsheet are provided below, and calculations for 13 ships are presented in Table 12.

Operating time.

$$T_O(hr) = \frac{A_W}{R_C}$$

A_W = *wetted area of ship* (ft^2)

R_C = *cleaning rate* (ft^2/hr)

Days of operation to complete the ship.

$$Days = \frac{T_O(hrs)}{6.5(hrs/day)}$$

Gallons treated.

$$V_E(gal) = T_O \times Q_E \times 60 \times f_s;\ Q_E = flowrate\ of\ AHMV\ (gpm)$$

Number of tanker cars required for effluent storage.

$$Tanks = \frac{V_E}{6{,}000(gal)}$$

Size of tanker is 6,000 gal

Tanks required per day.

$$\frac{Tanks}{Day} = \frac{Total\ tanks\ per\ cleaning}{Total\ days\ per\ cleaning}$$

Volume of paint removed during hull cleaning.

$$V_P(ft^3) = \frac{A_w \times t_p \times f_s}{12} \qquad t_P = paint\ thickness\ stripped\ during\ cleaning\ (in)$$

Weight of paint removed.

$$W_P(lb) = V_P \times 62.4 \times S.G. \qquad S.G. = specific\ gravity\ of\ paint$$

Quantity of cuprous oxide in paint.

$$CuO(lb) = \frac{W_P \times \%CuO}{100} \qquad \%CuO = percentage\ of\ CuO\ in\ the\ paint$$

Quantity of copper in paint.

$$Cu(lb) = \frac{Cu\ molecular\ weight}{CuO\ molecular\ weight} \times CuO(lb)$$

Concentration of total copper.

$$Cu(mg/L) = \frac{Cu(lb) \times \frac{10^6}{2.205}}{V_E \times 3.78}$$

Table 12. Calculations for Volume of Wastewater Generated and Theoretical Copper Concentrations.

	Paint Stripped (mils)		2				Time usage			30 percent	
	Cleaning Rate (ft^2/hr)		2,000				Flow rate (gpm)			200	
	Tanker Car Volume (gal)		6,000				Weight of Cu in CuO (%)			45	
Designation	Wetted area (ft^2)* A_W	Operating Time (hrs) T_O	Days Operating (6.5hrs/day)	Gallons Treated V_E	# of Tanker Cars	Tanks/Day	V_p (ft^3) paint	W_p (lb) paint	CuO (lb)	Cu (lb)	Cu (mg/L) (ppm)
CARRIERS											
Nimitz	159500	79.75	12.27	287100	48	4	7.98	1104.76	497.14	396.46	165.71
Kitty Hawk	141470	70.74	10.88	254646	43	4	7.07	979.88	440.95	351.65	165.71
CRUISERS											
Ticonderoga	37840	18.92	2.91	68112	12	4	1.89	262.09	117.94	94.06	165.71
Virgina	42390	21.20	3.26	76302	13	4	2.12	293.61	132.12	105.37	165.71
California	40260	20.13	3.10	72468	13	4	2.01	278.86	125.49	100.07	165.71
Belknap	34360	17.18	2.64	61848	11	4	1.72	237.99	107.10	85.41	165.71
Bainbridge	36365	18.18	2.80	65457	11	4	1.82	251.88	113.35	90.39	165.71
Leahy	33430	16.72	2.57	60174	11	4	1.67	231.55	104.20	83.10	165.71
Long Beach	52600	26.30	4.05	94680	16	4	2.63	364.33	163.95	130.75	165.71
DESTROYERS											
Kidd	37840	18.92	2.91	68112	12	4	1.89	262.09	117.94	94.06	165.71
Spruance	35745	17.87	2.75	64341	11	4	1.79	247.58	111.41	88.85	165.71
FRIGATES											
Oliver Perry	19850	9.93	1.53	35730	6	4	0.99	137.49	61.87	49.34	165.71
Knox	22645	11.32	1.74	40761	7	4	1.13	156.85	70.58	56.29	165.71

* Goldberg, R. S. *Wetted Surface Areas of Naval Ships by Class*", David Taylor Research Center, TM-15-82-113, Dec 1992.

The theoretical concentration of 166 mg/L for total copper on the spreadsheet is much higher than the particulate and dissolved concentration (sum) measured by Mobile Processing Technologies at 28.4 mg/L from Table 5. This large difference may be the result of the method used to collect the wastewater in the studies or the assumptions used to calculated the theoretical concentration of total copper. The theoretical concentration of copper will decrease if any of the assumptions decrease: the amount of paint removed during cleaning, the amount of the surface area cleaned, the cleaning rate of the AHMV, or the copper composition of the antifouling paint.

TREATMENT TECHNOLOGIES

Four treatment processes evaluated are microfiltration, ion exchange, dissolved air flotation (DAF), and biological systems. The four treatment processes were chosen for several reasons: some initial technical research by the Navy, a treatment feasibility study in 1995 by the Navy, and a solicitation for sources of processing equipment and expertise through the Commerce Business Daily. Specifically, the DAF system was evaluated because several of these systems are currently operating at Naval bases.

Four pierside treatment processes will be discussed as possible individual or a combination of treatment(s) to accomplish the required removal: ion exchange, dissolved air flotation (DAF), microfiltration, and living and non-living biological treatment. Ion exchange is a process that could achieve the levels required to discharge the clean wastewater into the surface waters, however, it would have to be preceded by a filtration or dissolved air flotation (DAF) system inorder to remove the solids in the wastewater to avoid fouling of the ion exchange resin. The DAF system is a process many shipyards use for other industrial waste streams and can achieve the levels required to discharge the pretreated wastewater into the sanitary sewer system. Microfiltration is filtration process that would be preceded by a macro filtration to remove the large particulates then, depending on the level of treatment required, the wastewater may have to be processed through an ion exchange resin to remove the dissolved copper before discharging into the surface waters. Lastly are live or nonliving biological systems that could achieve surface water limitations for the removal of copper.

Ion Exchange

Ion exchange is a treatment process used for the removal of dissolved ionic species from wastewater by exchanging an undesired ion for a saturated ion that is on the resin. The saturated ion is held by electrostatic forces to charged functional groups on the surface of the resin. Because the exchange occurs on the surface, ion exchange is an adsorption process. The type of resin selected depends on the contaminant to be removed. The saturated ion on the resin surface must have a similar charge as the ion to be removed (U.S. EPA 1986). Ion exchange is commonly used for the treatment of industrial wastewater removing metal ions and cyanide. The treatment is accomplished by using a charged resin that is in column reactors. For the removal of copper ions, the specific ion exchanger could be one of the following (Haas and Vamos 1995).

Diphenylthiourea	8-Hydroxyquinoline
Anthroanilic acid	*B*-Diketon
Ethylenediaminetetra-acetic acid	N-picolylamine
Phosphonic acid	Amidoxime

Phosphonic acid and anthroanilic acid are also listed as selective to zinc removal. The flow and cross section of an ion exchange column is shown in Figure 3 and the exchange process is shown in Figure 4.

At first, the exchange sites are saturated with H^+ ions then, as the resin comes in contact with the wastewater, the exchange sites are replaced with the higher affinity ion Cu^{2+}. Once all the H^+ ions have been replaced, the column is exhausted and will require regeneration with an acid such as hydrochloric or sulfuric acid. The Cu^+ ions will be overcome by the high concentration of H^- ions and the column will again become saturated with H^-. The additional H^+ ions in the wastewater will lower the pH and require a pH adjustment before discharging into the sanitary sewer or surface waters.

$$2(R^-)H^+ + Cu^{2+}{}_{(aq)} \longleftrightarrow (R^-)_2 Cu^{2+} + 2H^+{}_{(aq)}$$

(Haas and Vamos 1995)

R = *anionic charge on the resin*

H^- = *counterion from acid*

Cu^{2+} = *contaminant to be removed*

In order to save resin capacity and avoid fouling of the resin, the wastewater stream should be filtered to remove any solids. Ion exchange would be used as a polishing treatment process if the Navy desired to discharge the treated stream directly into the surface waters rather than into the sanitary sewer system.

Ion exchange has proven to be highly efficient and dependable for recovering metal bearing solutions. It is a compact treatment process which makes it attractive for the AHMV. The maintenance required on an ion exchange system is the maintenance required on its pumps, valves and piping. One costly requirement, however, is the regeneration chemicals and the disposal of the waste stream produced during a regeneration. In addition, there has been documented damage to resins caused from iron, manganese, and copper if sufficient concentrations of dissolved oxygen are present (U.S. EPA 1986). As shown in the subsequent design calculations, 550 gallons of hydrochloric acid would be required to regenerate the system designed. A regeneration site would be best constructed away from the piers or contracted to a regeneration service in order to save valuable pier space.

The waste stream could be sold to a manufacturer of the antifouling paint. For example, American Chemet Corporation is interested in the wastewater. American Chemet manufactures the antifouling paint and strictly uses recovered copper from other industries for their paint. They will test a sample of the waste stream to see if it is feasible for them to recover and use the copper from hull cleanings in their paint manufacturing process. They will not commit a price for the wastewater before receiving a sample to analyze (Bohlander 1996).

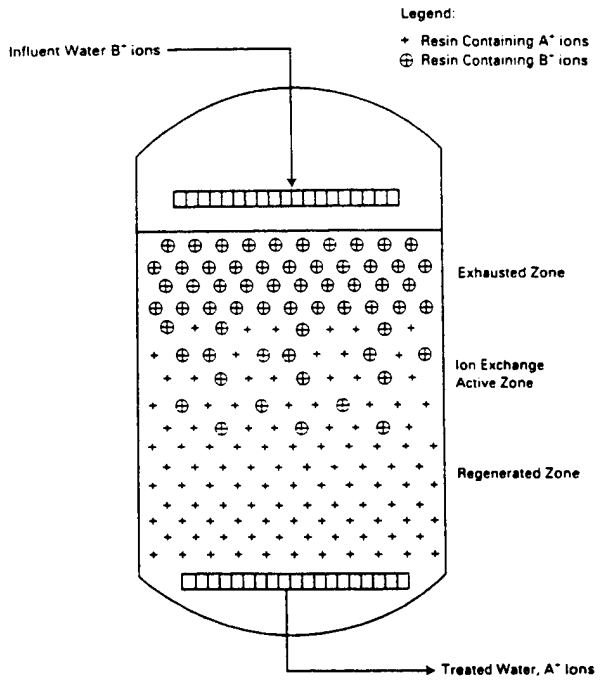

Figure 3. Ion Exchange Column in Service (Haas and Vamos 1995).
$A^{+}=H^{+}$ and $B^{+}=Cu^{2+}$

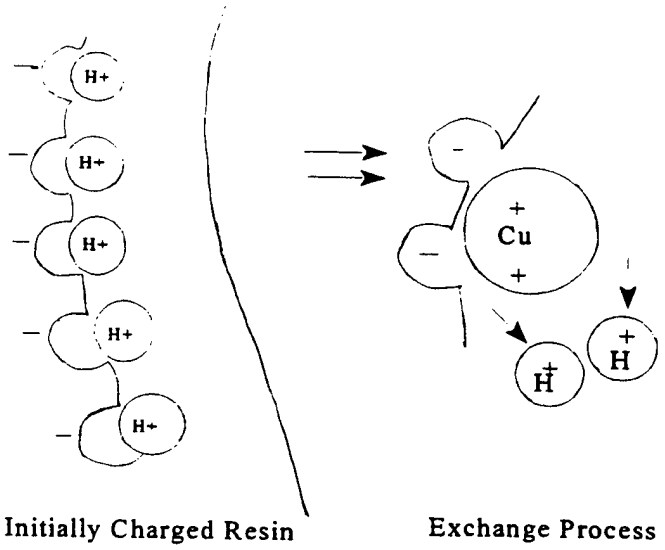

Figure 4. Exchange Sites on the Resin (Nuckols et al. 1994).

Design of a Ion Exchange System

Assumed parameters:

Flow rate of wastewater from AHMV	200 gpm
Dissolved Cu concentration	25 mg/L (assume 15% of total copper[3])
Resin	Ionac SR-5 (Sybron Chemicals Inc.)
Exchange capacity	36.9 eq/ft^3

The equivalents of copper that are in the wastewater from the AHMV per hour:

$$\frac{25\frac{mg}{L}\times\frac{g}{1000mg}\times 2\frac{eq}{mol}\times\frac{1000meq}{eq}}{63.5\frac{g}{mol}} = 0.787\frac{meq}{L}$$

$$0.787\frac{meq}{L}\times 200\frac{gal}{min}\times\frac{60min}{hr}\times\frac{3.785L}{gal}\times\frac{eq}{1000meq} = 35.75\frac{eq}{day}$$

The time required to treat effluent from the cleanings varies from 24 hours to as few as 3 hours. This cleaning time assumes the AHMV will be cleaning 30 percent of the operation time, while the AHMV takes and stores data the other 70 percent of the time. By selecting 24 hours as the time between regenerations, the system should only require to be regenerated every two weeks or more, and from Table 13 the system will also complete an aircraft carrier cleaning without a regeneration.

$$24hr\ treatment\times\frac{day}{6.5hrs\ operation}\times\frac{week}{5days}\times\frac{100hrs\ operation}{30hrs\ treatment}\cong 2.5weeks$$

Based on 24 hours between regenerations, the amount of resin required is for the ion exchange system:

$$35.75\frac{eq}{hr}\times 24hr\times\frac{ft^3}{36.9eq} = 23.25ft^3\times\frac{7.481gal}{ft^3}\cong 200gal$$

[3] Table 2-1 from the NASSCO study provided measurements for total and dissolved copper. The percent of dissolved copper ranged from 6.5 to 7.5. A safety factor of two is used for estimating the required resin since it is known that zinc will be in the effluent could take some of the exchange sites and since the percent of dissolved copper in the AHMV has not been determined.

In order to make this a mobile unit, arrange four 50 gallon drums or two 100 gallon drums of resin hooked-up in series on a skid mounted trailer. This would allow one drum at any time to be removed for regeneration.

The recommended loading of this resin is not known. However, from the Nuckols (1995) study, a contractor used a resin with a 16 Bed Volumes (BV) per hour maximum flowrate. At this loading, the design can treat the wastewater at a flowrate of 50 gpm.

$$16\ \frac{BV}{hr} \times \frac{200gal}{BV} \times \frac{hr}{60\,\text{min}} \cong 50gpm$$

Because the 200 gpm flowrate produced by the AHMV is not continuous, an equalization basin must provide the constant flowrate of 50 gpm. If a typical work day was 6.5 hours of actual operation of the AHMV, the amount of wastewater produced is 23,400 gal/day.

$$200\frac{gal}{\text{min}} \times \frac{6.5hr}{day} \times \frac{60\,\text{min}}{hr} \times 0.30 = 23{,}400\frac{gal}{day}$$

The equalization basin allows the treatment process to run continuous at a flow rate of 50 gpm and would have to operate for 8 hours per day.

$$23{,}400\frac{gal}{day} \times \frac{min}{50gal} \times \frac{hr}{60\,\text{min}} = \frac{8hr}{day}$$

The size of the equalization basin would depend on the volume of wastewater generated per hour. For the "best case" scenario, the AHMV would clean the same amount of time each hour (30 percent of 60 minutes), which would require a basin of about 4,000 gallons.

Amount of generated waste: $\frac{200gals}{min} \times \frac{60min}{hour} \times 30\% = \frac{3600gals}{hour}$

Amount of treated waste: $\frac{50gals}{min} \times \frac{60min}{hour} = \frac{3000gals}{hour}$

There is 600 gallons left at the end of each hour (3600 - 3000).

$$\frac{600gals}{hour} \times 6.5hours = 3{,}900gals$$

For a "worst case" scenario, the AHMV would clean 100 percent of the time for 30 percent of the daily operating time, which would require a basin of about 18,000 gallons.

$$23{,}400gals - \left(\frac{6.5hrs}{day} \times 30\% \times \frac{50gals\ treated}{min} \times \frac{60min}{hr}\right) = 17{,}550gals$$

The reason for a "worst case" scenario is there may be sections of the hull that are subject to extensive marine fouling while other sections have no marine fouling. Therefore, the cleaning brushes maybe operating for an extended period, instead of a steady 30 percent for each hour of operation.

The quantity of acid required using pure hydrochloric acid (HCl) is 9 lb HCl/ft^3 resin (Nuckols et al. 1994). Assuming a five percent solution, the quantity of HCl required can be calculated:

$$\frac{200gal}{bed\ resin} \times \frac{ft^3}{7.481gal} \times \frac{9lb\ HCl}{ft^3\ resin} \times \frac{100lb\ solution}{5lb\ HCl} = \frac{4812\ lb\ solution}{bed\ resin}$$

$$4812lb \times \frac{ft^3}{62.4lb \times 1.05} \times \frac{7.481gal}{ft^3} = \frac{550gal\ 5\%\ HCl\ solution}{regeneration\ bed\ resin}$$

See Table 13 for calculations of resin regeneration and HCl solution required per ship cleaning. Because the copper would be concentrated after regeneration, the copper in this waste stream might be economically feasible for recovery by American Chemet Corporation or other antifouling paint manufacturers. The amount of copper in the HCl solution is over 15000 mg/L.

$$200gal\ resin \times \frac{ft^3}{7.481gal} \times \frac{36.9eq}{ft^3 resin} \times \frac{mole}{2eq} \times \frac{63.5g\ Cu}{mole} = 31{,}321g\ Cu$$

$$31{,}321g\ Cu \times \frac{1}{550gal\ HCl\ solution} \times \frac{gal}{3.79L} \times \frac{1000mg}{g} = 15{,}026\frac{mg\ Cu}{L\ HCl\ solution}$$

Dissolved Air Flotation

Dissolved air flotation (DAF) is a five step process: add coagulant, slowly mix for flocculation, dissolve air in the wastewater under pressure, release the wastewater to atmospheric pressure and skim the floated sludge. DAF uses the attachment mechanism by affixing bubbles to the flocs that have been formed when the wastewater is released to atmospheric pressure. The efficiency of the system is dependent on the effectiveness of

Table 13. Calculations for Beds of Resin and Volume of Regeneration Acid per Cleaning.

	Paint Stripped (mils)		2		
	Cleaning Rate (ft^2/hr)		2,000		
	Time usage		30 percent		
	Flow rate (gpm)		200		
	5% HCl Solution for regeneration				
	Bed of resin exhausted in 24 hours				
Designation	Wetted area (ft^2)* A_W	Operating Time (hrs) T_O	Treatment Time (hrs) (30% of cleaning)	Fraction of Resin Bed Exhausted per cleaning	Gallons of 5% HCl per cleaning
CARRIERS					
Nimitz	159500	79.75	23.93	1.00	550.00
Kitty Hawk	141470	70.74	21.22	0.90	495.00
CRUISERS					
Ticonderoga	37840	18.92	5.68	0.24	132.00
Virgina	42390	21.20	6.36	0.27	148.50
California	40260	20.13	6.04	0.25	137.50
Belknap	34360	17.18	5.15	0.21	115.50
Bainbridge	36365	18.18	5.45	0.23	126.50
Leahy	33430	16.72	5.01	0.21	115.50
Long Beach	52600	26.30	7.89	0.33	181.50
DESTROYERS					
Kidd	37840	18.92	5.68	0.24	132.00
Spruance	35745	17.87	5.36	0.22	121.00
FRIGATES					
Oliver Perry	19850	9.93	2.98	0.12	66.00
Knox	22645	11.32	3.40	0.14	77.00

* Goldberg, R. S. *Wetted Surface Areas of Naval Ships by Class"*, David Taylor Research Center, TM-15-82-113, Dec 1992.

the coagulation and flocculation. The floc surface needs to be hydrophobic so the bubbles attach and float the flocs to the surface (Gregory and Zabel 1990).

Coagulation is the addition of a chemical in order to destabilized the particles and is necessary in order to form flocs. The flocs are formed when the electrostatic surface charge is reduced, causing the particles to stick together. Both the coagulating agent and the pH are important parameters to forming good flocs. Ferric sulfate is a common coagulant and lime is a common agent added to regulate the pH. Rapid, thorough mixing is an important step for both of these chemicals to be efficient (Nuckols et al. 1994).

Lime raises the pH while forming the copper hydroxides for precipitation. The dominant species at respective pH are listed below and demonstrate that the pH will have to be raised above 10.7 in order to precipitate the copper (Stumm and Morgan 1996).

Cu^{2+}	$pH \leq 6.0$
$CuCO_3(aq)$	$pH \geq 6.0 - 9.3$
$Cu(CO_3)_2^{2-}(aq)$	$pH \geq 9.3 - 10.7$
$Cu(OH)_3^-$	$pH \geq 10.7 - 12.9$
$Cu(OH)_4^{2-}$	$pH \geq 12.9$

The purpose of adding the chemicals is to form agglomerations of particles which are called flocs. Without forming the flocs, the flotation process will be inefficient or unable to remove colloid-size particles. Flocculation is slow, gentle mixing of the wastewater where the flocs form. The coagulation and flocculation steps are designed to specifically form flocs that will be suitable for flotation (Gregory and Zabel 1990).

Once coagulation and flocculation are completed, air is injected into the wastewater under a pressure of several atmospheres. It is held for several minutes in a retention tank allowing the air to dissolve in the wastewater. The wastewater is then released to atmospheric pressure. The sudden change in pressure causes the release of minute bubbles that attach to the flocs and float the suspended solids to the surface. On the surface, a skimmer is used to remove the floating sludge which is transferred to a dewatering system.

The clarified water is taken from the bottom of the tank and discharged either to the sanitary sewer system or, depending on permit standards, to local surface waters (Gregory and Zabel 1990). Figure 5 is a schematic diagram of an oily wastewater treatment plant where the Navy currently uses a DAF system. Figure 6 is a DAF system manufactured by Jalbert & Associates, Inc of Norfolk, VA and leased by the U.S. Navy.

The most important parameter for the DAF system is the volume of air to the mass of solids ratio, also known as the air-to-solids (A/S) ratio. This ratio represents the desired clarification and is very difficult to predict without bench testing or pilot plants. Wastewaters have different particulate matter and flotation is dependent on the surface of the particulate matter. The bench study will determine the solid matter that is floated as a function of air added (Tchobanoglous and Burton 1991).

The Navy currently has several DAF operating systems. These systems could save large sums of money by avoiding the initial capital investment cost, if the system can remove the copper to sanitary sewer limits for hull cleaning operations. With proper pH control, the Navy achieves effluent levels of copper below 50 μ g/L (O'Connor, 1996) and other full scale industrial DAF facilities report effluent levels of copper at 0.5 mg/L (Nuckols et al. 1994). The Naval Shipyard Norfolk can meet the NPDES permit limit with the DAF, allowing the Norfolk area to discharge the effluent into surface waters rather than into the sanitary sewer for further treatment. Although DAF is a reliable treatment system that provides a high level of solids separation, one disadvantage is the increased quantity of sludge resulting from the added chemicals.

Sludge generated from the DAF systems which the Navy operate is not hazardous material and can be disposed at local landfills (O'Connor, 1996). The sludge generated as a result of treating hull cleaning wastewater would have to be analyzed to determine if it is hazardous waste before proper disposal could be determined. Due to the amount of sludge generated from added chemicals, the concentration of copper in the sludge will probably make it less economically feasible to ship and to recover the copper by paint manufacturers.

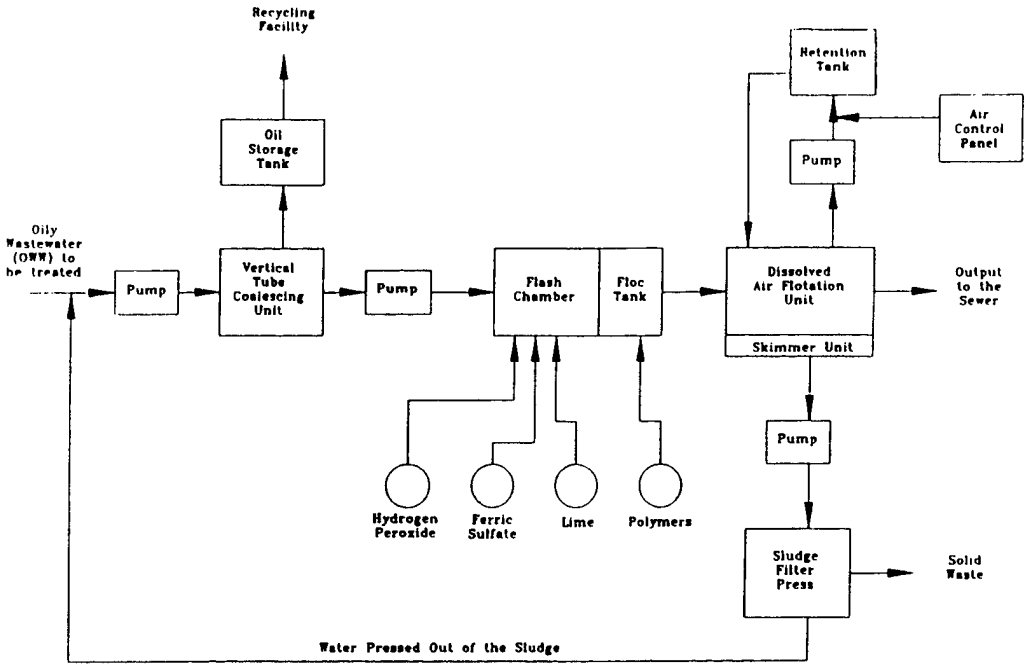

Figure 5. U.S. Navy Oily Wastewater Treatment Plant (Nuckols et al. 1994).

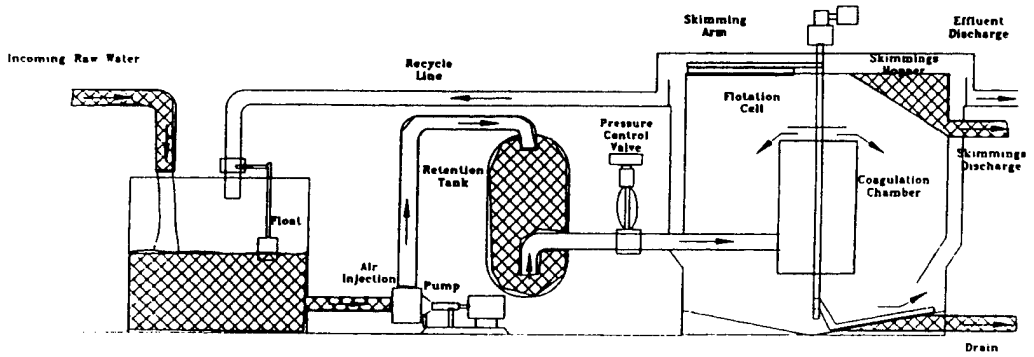

Figure 6. U.S. Navy DAF System, Full Flow Pressurization (Nuckols et al. 1994).

Crossflow Microfiltration

Reverse osmosis was not considered due to the cost required to operate at high pressures and the necessary pretreatment required to remove the suspended solids. In addition, ultrafiltration should not be necessary as a result of the Mobile Processing Technology experiment using a 11 μm filter that achieved nondetectable copper levels, as shown on Table 5. Therefore, microfiltration which filters particles larger than ultrafiltration is reviewed for the hull cleaning wastewater treatment.

Microfiltration is a pressure driven flow through a membrane which separates particles approximately 0.1 to 10 μm in size from fluids. The pressure drop across the filter is typically about 50 psi. The pressure differential causes the fluid and small species to pass through the membrane and collect as permeate while particles are retained by the filter and collected as concentrate (Davis 1992).

Crossflow microfiltration is illustrated in Figure 7. As shown in the figure, the feed flows tangential to the surface of the microporous membrane wall while the pressure drop causes a crossflow of permeate through the membrane. Particles are transported across the membrane surface forming a thin cake layer. Because the tangential flow causes a shear force, the cake does not build up, but instead sweeps the particles toward the filter exit (Davis 1992).

The disadvantage of crossflow microfiltration is the high energy consumption resulting from the high pumping volumes. As a result of the high energy usage, the technology has been limited to high-value materials such as beer, fruit juices and milk processes. However, with the development of a ceramic membrane with star-shape tubular channels, this shape has reduced the cross-sectional area and volume by fifty percent. The velocity remains the same in order to sweep the particles away, but less energy is required to pump the wastewater since the flowrate has been reduced. The ceramic membrane may be a cost effective alternative for medium to low-value processes such as the hull cleaning wastewater (Fairey Industrial Ceramics 1993).

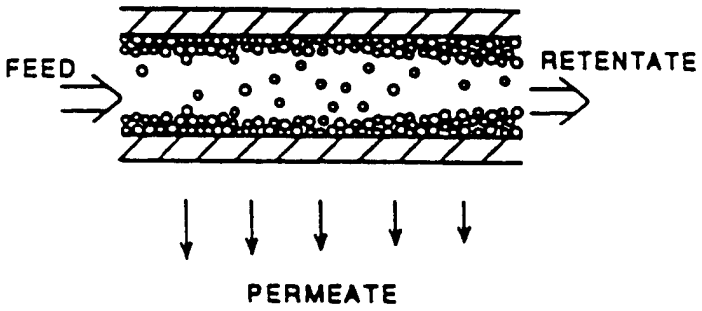

Figure 7. Crossflow Microfiltration (Davis 1992).

Microfiltration will likely remove all particulate copper and the wastewater could be discharged into a sanitary sewer system. However, if the permeate is discharged directly into the surface waters, a treatment process would have to proceed the microfiltration in order to remove the dissolved copper. For example, microfiltration could precede ion exchange.

The concentrate from the crossflow microfiltration should be considered for recycling by the antifouling paint manufacturers , but may not be feasible due to the levels of other particles in the waste. If not feasible for recycling, the waste stream should be tested to determine if it a hazardous waste and disposed of accordingly.

Biological Systems

Biological systems were investigated for several reasons: their lack of binding affinity to earth metal cations, such as, magnesium, sodium, potassium and calcium; their ability to achieve high efficiency for metal removal; their ability for repeated regeneration and their potentially low cost and low maintenance (Brierley et al. 1989).

Algal Turf Scrubber (ATS™)

Algal turf scrubbing is a live biological process which has been successfully applied in the purification of chronically-polluted waters. It has a demonstrated capability to remove a variety of heavy metals and organic and inorganic substances to undetectable levels from polluted waters. The most significant mechanism the ATS™ uses to remove

the metals is adsorption wherein the walls of the algae are negatively charged due to the presence of carboxyl, hydroxyl and phosphoryl sites, which have negative charges to attract the positively charged metals. The cations rapidly bind without any added energy (Craggs et al. 1996).

The system is designed to bring secondary sewage to tertiary levels. Following a four year pilot plant study, the system was approved in Patterson, California and full scale construction is currently underway. The design of the California system focused on nitrogen removal. In addition, a 43 acre system is scheduled to be constructed in Florida early in 1997 and, lastly, the city of Fruitland, Maryland, in cooperation with the State of Maryland, is currently designing a pilot plant focusing on phosphorus and nitrogen removal.

The State of Maryland has required the city of Fruitland to accomplish three objectives with the ATS™.

- Discharge levels: phosphorus not to exceed 2 mg/L and nitrogen not to exceed 8 mg/L.
- Utilization of the by-products, i.e. harvested algal turf rich in nutrients.
- Satisfy permit requirements for discharge, for sludge utilization when using it for stabilization/bulking agent on poor soil, and for sludge utilization when using it as fish food.

The size of the turf will be 250 feet by 20 feet and will treat 12,500 gallons per day. The stream will be pulled off the effluent of Fruitland's 1 mgd wastewater treatment plant. The city will be required to test the harvested algal turf for all contaminants to confirm levels of heavy metals or other constituents that may cause problems in the utilization of the by-products. The schedule calls for construction to begin in September 1996 and processing in October 1996 (Roderick 1996).

A bench scale study was completed on contaminated groundwater from a New Jersey industrial site using the ATS™ with artificial lighting (metal halide lights). The bench study was successful in removing organic compounds such as trichloroethylene, vinyl chloride and acetone and in removing inorganic compounds such as magnesium, iron and manganese (Adey et al. 1995).

The advantages and disadvantages of using the ATS™ system to treat the wastewater generated from the AHMV have been identified. The ATS™ system is both inexpensive (costing only $1/gallon of daily capacity for capital investment) and low tech (needing only sunlight, wastewater and occasional harvesting).

However, there are more potential disadvantages if the system is used for the AHMV. According to the manufacturer (Aquatic BioEnhancement Systems), the area required for removal of copper from about 1 mg/L to <2 μg/L is 3000 m^2 for the summer and 6050 m^2 for the winter. The difference is due to the reduced sunlight available during the winter which makes it less efficient for removal of contaminates. At this large size, the system simply could not fit on most Navy piers and even if the system could fit on a pier, it would be very difficult to demobilize/mobilize to make room for higher priority pier business. Furthermore, the system may not meet removal requirements on rainy or cloudy days because of reduced sunlight which will disrupt the hull maintenance contractor's schedule. Also, the system needs to be used about every three days in order to sustain the algae (Adey 1996). If the three day requirement can not be meet, maintenance costs will increase during non-hull cleaning periods and, if the system is neglected for long periods of time, potentially all capital investments could be lost.

Consideration was given to stacking strips of the turf and applying artificial lighting, however, the initial cost and continuing costs would dramatically increase total costs. A more detailed cost analysis ought to be undertaken to judge the ATS™ with artificial lighting to alternative treatments.

This system would be best applicable at a permanent treatment facility where maintenance workers make regular checks and the system is consistently used. A Navy facility that could make good use of the algal turf scrubber is a Naval Shipyard which has a variety of waste streams. It is felt other processes are more feasible for the AHMV.

Nonliving Biological Systems

When evaluating the disadvantages of the ATS™ system, the application of a nonliving systems appears to be more feasible for the AHMV system. Nonliving systems use biomass in a column in a form that is similar to ion exchange resins or activated carbon. The columns can be mobilized by mounting them on skid trailers. The system would not be dependent on weather, could be cost-effective, and does not require consistent use.

Advanced Mineral Technologies, Incorporated, in Golden, Colorado has developed stable, spherical granules by immobilizing *Bacillus* species. The granules are either packed bed, expanded bed or dispersed bed columns. When wastewater enters the column, the biomass expands, becomes porous and metals "bind" throughout the granule. Unlike biological systems the granules do not "capture" calcium, sodium, potassium or magnesium but leave the pore spaces for the hazardous metals. The columns perform regardless of metal influent concentrations; at greater than 99 percent efficiency and produce effluents as low as 10-50 μ m/L Also, the granules can be regenerated by applying electrowinning technology with the use of electrolytes (Brierley et al. 1989).

ECONOMIC ANALYSIS

The following economical analysis is completed on three alternatives for treating the waste to different levels of treatment; no treatment, treatment to sanitary sewer limits and treatment to NPDES limits. This analysis is completed using prices and quantities known from Norfolk, Virginia. All interest table values were taken from the Donald G. Newnan textbook (1996).

Assumptions made:

- Flowrate = 200 gpm
- AHMV operation = 6.5 hrs/day
- Number of days per hull cleaning = 3 days
- Average number of ships cleaned per year at Norfolk = 29

- The costs to bring the waste pierside are not dependent on the treatment technology. Therefore, this cost will not be included.
- The costs for an equalization basin or holding tank are not dependent on the treatment technology. Therefore, this cost will not be included.
- The costs for sampling and lab work are not dependent on the treatment technology. Therefore, this cost will not be included.
- The analysis will be for 20 years, since this is the estimated salvage value for both the DAF and filtration/ion exchange.
- An interest rate of 3% will be used, since this is the interest rate DoD has established for all economic analysis during fiscal year 1997.
- Waste generated per day is 25,000 gal/day.

  Waste Generated per Day

$$\frac{200gal}{\min} \times \frac{6.5hrs}{day} \times \frac{60\min}{hr} \times 30\% = \frac{23{,}400gal}{day}; \quad say \quad \frac{25{,}000\ gal}{day}$$

- The wastewater has total suspended solids of 200 mg/L, and the concentrate from the microfiltration is 1.5 percent solids with a specific gravity of one.
- Copper from the regeneration waste of ion exchange is recoverable. Assume the Navy neither incurs costs nor receives benefits from this waste.
- All annualized costs and net present worth costs are rounded to the nearest thousands.

Option 1: Disposal by Trucking the Wastewater to Offsite, Non-Navy Treatment Facility.

Costs:

- *Rental of 6,000 gal truck with driver - $200/day (Lee 1996)*
- *Cost of Treatment by commercial facility - $0.25/gal (Lee 1996)*

A. Trucking cost

$$\frac{29\ hull\ cleanings}{year} \times \frac{3days}{hull\ cleaning} \times \frac{2trucks}{day} \times \frac{\$200}{truck} = \frac{\$34{,}800}{year}$$

B. Treatment cost

$$\frac{29\ hull\ cleanings}{year} \times \frac{3days}{hull\ cleaning} \times \frac{25{,}000gals}{day} \times \frac{\$0.25}{gal} = \frac{\$543{,}800}{year}$$

Annualized Costs: $34,800 + $543,800 = $579,000

Net Present Worth: $578,600(P/A, 3%, 20) = 578,600 x 14.778 = $8,551,000

Option 2 (a): Disposal into the Sanitary Sewer System Using a DAF Treatment Facility.

Costs for leasing:

- *Daily lease cost of DAF with operator - $240/day (Jalbert & Associates 1996)*
- *Cost of Treatment for the contractor to operate the DAF, inclusive of everything - $0.03/gal (Jalbert & Associates 1996)*
- *Cost to publicly owned treatment works (POTW) for further treatment - $3.5/1000gal (Lee 1996)*

A. Leasing cost

$$\frac{29\ hull\ cleanings}{year} \times \frac{3days}{hull\ cleaning} \times \frac{\$240}{day} = \frac{\$20{,}880}{year}$$

B. Treatment cost

$$\frac{29\ hull\ cleanings}{year} \times \frac{3days}{hull\ cleaning} \times \frac{25{,}000gals}{day} \times \frac{\$0.03}{gal} = \frac{\$65{,}250}{year}$$

C. Cost for sanitary sewer disposal

$$\frac{29\ hull\ cleanings}{year} \times \frac{3days}{hull\ cleaning} \times \frac{25{,}000gals}{day} \times \frac{\$3.5}{1000gal} = \frac{\$7{,}613}{year}$$

Annualized Costs: $20,880 + $65,250 + 7,613 = $94,000

Net Present Worth: $93,743(P/A, 3%, 20) = 93,743 x 14.778 = $1,385,000

Option 2 (b): Disposal into the Sanitary Sewer System Using a DAF Treatment Facility.

Costs for purchase and operation:

- *Initial cost of DAF - $320,000 (O'Conner 1996)*

- *Cost of Treatment for the Navy to operate the DAF, inclusive of everything - $0.05/gal (O'Conner 1996)*
- *Cost to POTW for further treatment - $3.5/1000gal (Lee 1996)*

A. Treatment cost by the Navy

$$\frac{29\ hull\ cleanings}{year} \times \frac{3days}{hull\ cleaning} \times \frac{25{,}000gals}{day} \times \frac{\$0.05}{gal} = \frac{\$108{,}750}{year}$$

B. Cost for sanitary sewer disposal

$$\frac{29\ hull\ cleanings}{year} \times \frac{3days}{hull\ cleaning} \times \frac{25{,}000gals}{day} \times \frac{\$3.5}{1000gal} = \frac{\$7{,}613}{year}$$

Annualized Costs: $320,000(A/P, 3%, 20)+$108,750+$7,613

$320,000(0.0672)+$108,750+$7,613 =$138,000

Net Present Worth: $320,000+$116,363(P/A, 3%, 20) = $320,000+116,363 x 14.778

= $2,040,000

Option 3: Disposal into the Surface Waters Using Crossflow Filtration and Ion Exchange Treatment.

Costs for purchase and operation:

- *Initial cost of the system - $500,000 (Kelly 1996)*
- *Annual maintenance - 3% of capital investment (Kelly 1996)*
- *Sludge disposal in landfill - $40/ton (Lee 1996)*
- *Chemical costs $290/55 gal of 31% HCl (Arcal Chemical 1996)*
- *Specific Gravity of 31% HCl is 1.18 (Arcal Chemical 1996)*
- *Every 3 years replace resin at $350/ft^3 (Kelly 1996)*
- *Every 7 years replace filter at $30,000 (Kelly 1996)*
- *Operator at $25/hr (Kelly 1996)*

A. Annual maintenance cost

$$\frac{0.03}{year} \times \$500{,}000 = \$15{,}000$$

B. Sludge disposal

$$\frac{0.25 \times 200}{0.015} = \frac{3333 gal(wet\ sludge)}{day} \times \frac{ft^3}{7.48 gal} \times \frac{62.4 lbs}{ft^3} = \frac{27{,}800 lbs}{day}$$

$$\frac{27{,}800 lbs}{day} \times \frac{ton}{2000 lbs} \times \frac{\$40}{ton} = \frac{\$556}{day} \times \frac{29\ hull\ cleanings}{year} \times \frac{3 day}{hull\ cleaning} = \frac{\$48{,}370}{year}$$

C. Chemical costs (HCl)

$$\frac{200\ gal\ resin}{bed\ resin} \times \frac{ft^3}{7.48\ gal} \times \frac{9 lbHCl}{ft^3 resin} \times \frac{100 lb\ solution}{31 lb\ HCl} = \frac{776 lb\ solution\ (31\%)}{regeneration}$$

$$\frac{776\ lb\ solution\ (31\%)}{regeneration} \times \frac{regeneration}{24 hrs} \times \frac{6.5 hrs}{day} \times \frac{29 hull\ cleanings}{year} \times \frac{3 days}{hull\ cleaning}$$

$$= \frac{18{,}290 lb\ solution\ (31\%)}{year} \times \frac{ft^3}{62.4 lbs \times 1.18} \times \frac{7.48 gal}{ft^3} \times \frac{\$290}{55 gal} = \frac{\$9797}{year}$$

D. Operator cost

$$\frac{29\ hull\ cleanings}{year} \times \frac{3 days}{hull\ cleaning} \times \frac{8 hrs}{day} \times \frac{\$25}{hr} = \frac{\$17{,}400}{year}$$

Annual operating costs:

Maintenance	= $15,000
Sludge	= $48,370
Chemical	= $ 9,797
Operator	= $17,400
Total	= $90,567

Total NPW of annual operating costs = $90,567 x 14.877 = $1,347,400

Resin Replacement

$$\frac{\$350}{ft^3 resin} \times \frac{200 gal\ resin}{bed} \times \frac{ft^3}{7.481 gal} = \frac{\$9357}{bed} (replace\ every\ three\ years)$$

NPW year 3 = 9357 x 0.9151=8563

NPW year 6 = 9357 x 0.8375=7836

NPW year 9 = 9357 x 0.7664=7171

NPW year 12 = 9357 x 0.7014=6563

NPW year 15 = 9357 x 0.6419=6006

NPW year 18 = 9357 x 0.5874=5496

Total NPW of Resin = $41,635

Filter Replacement

NPW year 7 = 30,000 x 0.8131=24393

NPW year 14 = 30,000 x 0.6611=19833

Total NPW of Filter = $44,226

Net Present Worth: $500,000+$1,347,400+$41,635+$44,226 = $1,933,000

Total Annualized Costs: $1,933,261(A/P, 3%, 20) = 1,933,261 x 0.0672 = $130,000

Table 14. Summary of Economic Analysis for Norfolk, Virginia.

Analysis	Treatment Costs (Dollars)			
	DAF lease	**Filter/IER**	**DAF purchase**	**Trucking**
Annualized Cost	94,000	130,000	138,000	579,000
Net Present Worth	1,385,000	1,933,000	2,040,000	8,551,000

From the analysis, it can be concluded that leasing the DAF system is the most cost effective system. In addition, this analysis did not consider the management cost for permits and the possible penalties the Navy might incur if a NPDES permit is not met for the ion exchange system or if a POTW permit is not met for the DAF system. But, both the management costs and penalties would most likely make the difference in cost of the microfiltration/ion exchange and DAF systems even greater. In addition, the Navy already has experience with DAF systems at locations where a large percentage of hull cleaning activities take place. This could make the DAF an even more effective and reliable system for the Navy. Lastly, the analysis does provide the data which indicates that trucking the waste to commercial facilities is unreasonable as a Navy-wide, long term solution. But, this option could be the most effective for remote, one-time hull cleanings.

RECOMMENDATIONS

The following are recommendations to further the development of a treatment system for the AHMV effluent. After reviewing the available studies and their conclusions and my own independent research, these recommendations represent my best professional opinion as to the order in which further studies should be pursued.

- Complete more field studies to characterize the wastewater by collecting and analyzing pierside during hull cleaning operations. The wastewater characterization is critical for determining the most cost-effective treatment.
- Have a short term plan to treat the to effluent levels acceptable for sanitary sewers while working on a long term plan to discharge in the harbor. During the short term phase, pilot plants could provide data and achievable levels for future UNDS regulations or NPDES permit negotiations.
- Undertake a study on the existing treatment facilities the Navy operates or has existing collection hook-ups at all the sites where underwater hull cleaning operations could take place.
- Undertake a study on microfiltration to determine the most cost-effective microfilter which will treat the effluent to sanitary sewer acceptable levels.
- Undertake additional toxicity studies on the bioavailability of copper from hull cleanings. These studies will provide backup data when writing UNDS or negotiating permits.

CONCLUSION

If the U.S. Navy continues to use a cuprous oxide antifouling paint on ships, it is clear that the generated wastewater during hull cleaning operations will eventually be regulated. The regulations may be established by the UNDS or by the current EPA water limits for copper. All studies completed to date show that the generated wastewater

exceeds all discharge limits for dissolved copper, including, the current EPA water limit, the NPDES permits managed by the Navy and the sanitary sewer limits required on naval bases. Therefore, treatment to reduce the dissolved copper in hull cleaning wastewater will be required regardless of which manner the regulations are formed and which level of discharge the U.S. Navy selects.

If the local sanitary treatment plants will accept the effluent from the DAF, this appears to be the best solution for three reasons: the Navy currently operates the DAF system, the DAF system has shown to consistently meet sanitary sewer discharge limits, and according to the results of this paper, the DAF system is the most economical alternative for almost 40 percent less than the microfiltration/ion exchange.

However, further studies should be undertaken to better characterize the wastewater. These studies will be important in testing new and existing technologies so that the most economical and environmentally benign process will be pursued.

Appendix A

Courtaulds Coatings, Inc.
[illegible] Antoine Drive
[illegible], TX 77210-4806

Courtaulds Coatings, Inc.
2270 Morris Avenue
Union, NJ 07083-0586

MATERIAL SAFETY DATA SHT

May be used to comply with OSHA's Hazard Communication Standard 29CFR 1910. 1200.
(THIS MSDS SUPERCEDES ANY PREVIOUS ISSUE)
PLEASE DIRECT TO THE APPROPRIATE DEPARTMENT IMMEDIATELY

Telephone No.: (713) 932-1711
Emergency Telephone No.: (713) 932-1711
Date of Preparation: 11/07/90
Our Reference: T3919114/AD/39

SDS
M 4996 #
NSWC, Carderock Division
Annapolis Detachment

tion One: Product Identification

Prod. No. 8RA640
Prod. Name INTERVIRON ANTI-FOULING RED
Prod. Class N/A

Section Two: Hazardous Ingredients

		% Wt. (optional)	Occupational Exposure TLV	Occupational Exposure PEL	Va (m (@
*	N-BUTYL ALCOHOL	1-5	50.00 PPM	50.00 PPM	
71-36-3	1-BUTANOL	10-15	100.00 PPM	100.00 PPM	
*	XYLENE	40-45	1.00 MG/M3	1.00 MG/M3	
1330-20-7	DIMETHYLBENZENE	1-5	N/A	N/A	
*	CUPROUS OXIDE	15-20	5.00 MG/M3	5.00 MG/M3	
1317-39-1	COPPER OXIDE (CU2O)				
	POLYAMIDE RESIN				
68650-50-0	POLYAMIDE RESIN				
*	ZINC OXIDE				
1314-13-2	ZINC OXIDE				

* CHEMICALS SUBJECT TO THE REPORTING REQUIREMENTS OF SECTION 313 OF THE EMERGE PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT OF 1986, AND OF 40 CFR 372.

N/A Not Available

Section Three: Physical Data

Boiling Range 244-280 DEG. F Vapor Density Heavier than air [X] Lighter than air [ ]
Evaporation Rate: Faster than either [ ] Slower than either [X] Volatile Weight (Theoretical) 15 LB/Gal. 13.3

Section Four: Fire and Explosion Hazard Data

Flammability Classification: OSHA: FLAMMABLE, CLASS I C DOT: FLAMMABLE
Flash Pt. 80 DEG. F (ASTM D3278-78) LEL. 1.0 PERCENT BY VOLUME
Extinguishing Media Foam [X] "Alcohol" Foam [ ] CO2 [X] Dry Chemical [X] Waterfog [ ] Other

Unusual Fire and Explosion Hazards

CONTAINS FLAMMABLE SOLVENT. DO NOT USE IN AREAS WHERE SPARK OR OPEN FLAME ARE PRESENT.

Special Fire Fighting Procedures

SMOTHER FLAMES WITH ONE OF THE ABOVE EXTINGUISHING MEDIA. WATER MAY BE USED TO COOL UNOPENED CONTAINERS, BUT MUST NOT BE USED AS AN EXTINGUISHING MEDIA. TAKE CARE TO PREVENT SPREAD OF BURNING LIQUID WITH WATER. CLOSED CONTAINERS MAY EXPLODE WHEN EXPOSED TO EXTREME HEAT.

Section Five: Health Hazard Data

ERA640 T3919114/A0/39

Effects of Overexposure

EYES - SEVERE IRRITATION,REDNESS,TEARING AND BLURRED VISION.
SKIN - IRRITATING. MAY RESULT IN DERMATITIS.
HARMFUL IF ABSORBED THROUGH SKIN.
INHALATION - SEVERE IRRITATION,DIZZINESS,POSSIBLE NAUSEA AND VOMITING AND UNCONSCIOUSNESS.
INGESTION - GASTROINTESTINAL IRRITATION,NAUSEA,VOMITING, DIARRHEA AND UNCONSCIOUSNESS.

Medical Conditions Prone To Aggravation By Exposure

SKIN AND RESPIRATORY CONDITIONS.

Ingredient Listed as Carcinogen or Potential Carcinogen NTP NO ARC Monographs NO OSHA NO

Primary Routes) of Entry: Dermal [X] Inhalation [X] Ingestion [ ]

Emergency and Fits Aid Procedure

EYES - FLUSH IMMEDIATELY WITH COPIOUS QUANTITIES OF WATER FOR 15 MINUTES.GET MEDICAL ATTENTION IMMEDIATELY.
SKIN - REMOVE CONTAMINATED CLOTHING,WASH SKIN WITH PLENTY OF SOAP AND WATER. LAUNDER CLOTHES BEFORE REUSE.
INHALATION - REMOVE TO FRESH AIR.GIVE ARTIFICIAL RESPIRATION IF NEEDED.GET MEDICAL ATTENTION.
INGESTION - GET MEDICAL ATTENTION IMMEDIATELY.DRINK PROMPTLY MILK,EGG WHITES,GELATIN SOL'N OR WATER.AVOID ALCOHOL.

Section Six: Reactivity Data

Stability Unstable [ ] Stable [X] Hazardous polymerization May occur [ ] Will not occur

Hazardous Decomposition Products

CO,CO2,VARIOUS HYDROCARBON FRAGMENTS
ZINC FUMES COPPER FUMES

Conditions To Avoid

KEEP DRY.
KEEP AWAY FROM DIRECT HEAT,FLAME OR SPARK.

Incompatability (Conditions To Avoid)

MOISTURE
OXIDIZING AGENTS

Section Seven: Spill or Leak Procedure

Steps to be taken if material is released or spilled: Remove all sources of ignition. Avoid inhalation of vapors. Ventilate area. Clean up with absorbant materials

Waste Disposal Method: Dispose in accordance with local, state, and federal regulations. Do not incinerate unopened containers.

Section Eight: Safe Handling and Use Information

Respiratory Protection: In outdoor or open areas, with unrestricted ventilation; use a NIOSH approved filter respirator to remove solid air-borne particles of overs during spray application. In restricted ventilation areas, use a NIOSH approved respirator in accordance with 29 CFR 1910. 134 to remove a combination of partic and vapors.

Ventialtion: Provide sufficient ventilation, in volume and pattern, to keep TLV and LEL of hazardous ingredients below limits specified on page one, and to re- decomposition products during welding or flame cutting on surfaces coated with this product.

Protective Gloves: Wear chemical resistant gloves.

Eye Protection: Safety glasses, chemical goggles, and/or face shield should be worn to prevent eye contact.

Hygienic Practices: Remove and wash soiled clothing before reuse; Wash hands before eating or smoking.

Other Protective Equipment

WEAR APPROPRIATE IMPERVIOUS PROTECTIVE CLOTHING TO PREVENT SKIN CONTACT.

Section Nine: Special Precautions

Precautions to be Taken in Handling and Storing

STORE IN BUILDING DESIGNED AND PROTECTED FOR STORAGE OF LIQUIDS WITH NFPA CLASS GIVEN BY OSHA CLASS IN SECTION 4.
AVOID BREATHING DUST OR CHIPS FROM SANDING OR BLASTING SURFACES COATED WITH THIS PRODUCT.

Recommended Grounding and Bonding of Containers When Transferring Liquids and Powders To Avoid Static Charge Build Up.

Other Precautions:

CHRONIC OVEREXPOSURE TO, AND MISUSE OF, SOLVENTS HAS BEEN LINKED TO PERMANENT BRAIN AND NERVOUS SYSTEM DAMAGE.
INHALATION OF ZINC FUME MAY PRODUCE SYMPTOMS KNOWN AS METAL FEVER. SYMPTOMS USUALLY DISAPPEAR WITHIN 24 HOURS.
THIS MATERIAL IS TOXIC TO FISH IF MISUSED,READ CONTAINER LABEL BEFORE USE.

The information contained herein is based on the data available to us and is believed to be correct. However, Courtaulds Coatings, Inc. makes no warranty, expressed or implied, regarding the accuracy of these data or the results to be obtained from the use thereof. Courtaulds Coatings, Inc. assumes no responsibility for injury from the use of the data described herein. Consult Courtaulds Coatings, Inc. for more information.

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